Semiannual Status Report

NASA Research Grant NsG-343, to the

University of Southern California

June 1, 1967

Prepared by R. Simha

R. A. Haldon, P. Rawlings and W. J. Schell

1. Multiple Transitions in Various Polymer Systems

Length-temperature measurements on a polyalkyl methacrylate series, between -180°C and the glass temperature, given in a previous Report, have been extended to longer chain polymers. Poly n-hexyl and n-octyl methacrylates behaved in a similar manner to the shorter side chain polymers, exhibiting three $T < T_g$ transitions in the temperature range studied and having expansion coefficients which increase with side chain length to values in excess of twice those observed for polymethyl methacrylate. The locations of the upper two T_{gg} transitions, parallels the main glass transition, decreasing with increasing side chain length. Poly n-decyl methacrylate shows only one obvious g-g transition, and lower expansion coefficients. This is probably due to ordering in the n-alkyl side chain, which restricts the glassy state motion somewhat.

A similar polyvinyl alkyl ether series has been studied in the same temperature range, yielding similar results to those obtained for the methacrylates. T_g decreases with increasing side chain length to n-octyl, and the polymers with a side chain longer than methyl exhibit one g-g transition in the temperature range T_g to $(T_g -70°C)$, with evidence of another at the limit of our present temperature range. Polyvinyl sec-butyl and iso-butyl ethers show two T_{gg} transitions and we suggest that this second transition is present in all the vinyl ethers below our temperature range. The glassy state expansion coefficients increase on lengthening the alkyl side chain, with a maximum at n-butyl, and thereafter decrease slightly. This again is believed due to ordering in the side chain which restricts motion. In this series the side chain shows a crystalline melting point when only ten carbon atoms long. The Simha-Boyer free volume product, $3(\alpha_\ell' - \alpha_g') \cdot T_g$, decreases with increasing

side chain length, as for the methacrylates, and substitution of α_g', , the
expansion coefficient below the g-g transition, for α_g' in their equation, gives
a value still too low. Again this suggests a transition below our current tem-
perature range.

Length-temperature measurements have also been made on a copolymer series
of tetrafluoroethylene (TFE) and 3,3,3 trifluoropropylene (TFP) of TFE content
0, 19, 42, 64 and 100 mole percent, between -185°C and T_g. This work has
yielded a pattern of $T < T_g$ transitions and each of these in the copolymers can
be associated with one in the parent homopolymer. PTFE (52% crystalline) has
a very broad transition, spanning about 50°, with its mid-point at about -100°C,
a smaller one at -37°C and a first order transition at 24°C. The two lower
transitions are present in all three copolymers, with their magnitude, given
by the difference in expansion coefficients above and below each transition,
decreasing with decreasing TFE content. Poly 3,3,3 trifluoropropylene exhibits
two $T < T_g$ transitions at -9 and -87°C. The former is also present in the two
copolymers of highest TFP content, with its magnitude dependent on the TFP
present. The transition at -87°C is in a similar location to the -100°C TFE
transition, with the latter making the larger contribution to the change in
expansion coefficient.

The copolymer glass temperatures extrapolate to a T_g for 100% amorphous
PTFE of 11-16°C, where no transition is seen for the homopolymer. In contrast
to T_g, $T_{gg}(i)$ do not vary with composition but are characteristic of the
intrinsic grouping, with only the magnitude of the effect depending on composi-
tion. The persistence of the transitions, even in low concentration of a
particular monomer unit, confirms that they correspond to motions of short
backbone segments, at least for those associated with TFE.

The thermal expansivity equipment has been modified for use to liquid

helium temperatures and work is currently in progress on the polyalkyl methacrylates and vinyl alkyl ethers between 4.2 and 77°K.

2. Equation of State Properties

Fürth's nearest neighbor distribution function[1], which we have been exploring as an alternate to the hole theory of the Equation of State, has been modified for the case of a simple monomer fluid, allowing the use of an electronic computer to evaluate its properties. The theory contains three parameters whose values cannot be determined by independent measurements to the accuracy required for reliable predictions of the thermodynamic properties. Consequently, the success of the theory depends on how well its predictions agree with experimental data when the precise values of the parameters are determined by a least square error analysis. At present we are engaged in such an error analysis using experimental compressibility isotherms for argon in the thermal region around the critical temperature.

An attempt has also been made since the last Report to extend Fürth's theory to polymer fluids and to mixtures of simple monomer fluids. However the rigorous formulae have not as yet been put into a form such that their predictions can be compared with the hole theory or with experiment.

REFERENCE

1. R. Fürth, Proc. Roy. Soc. Edin. 66A, 232 (1963-64).